SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED	1b RESTRICTIVE MARKINGS: NONE
SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release. Distribution unlimited.
DECLASSIFICATION/DOWNGRADING SCHEDULE	
PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 16	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: Massachusetts Institute of Technology / 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION: ONR
6c ADDRESS (City, State, and ZIP Code): 77 Massachusetts Avenue, Room 1-306 Cambridge, MA 02139	7b ADDRESS (City, State, and ZIP Code): 800 North Quincy Street Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION: DARPA / 8b OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-86-K-0[illegible]3
8c. ADDRESS (City, State, and ZIP Code): 1400 Wilson Boulevard Arlington, VA 22209	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. R & T Code / PROJECT NO. A 400005 / TASK NO / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
MOLECULAR DYNAMICS SIMULATION OF ATACTIC POLY(PROPYLENE) STRUCTURAL DIFFERENCES BETWEEN THE LIQUID AND GLASSY STATE

12. PERSONAL AUTHOR(S)
Mark F. Sylvester, Sidney Yip, and Ali S. Argon

13a. TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Abstract	FROM 1988 TO 1989	1989, May 29	2

16. SUPPLEMENTARY NOTATION
Abstract of oral presentation to be made at the American Chemical Society Symposium on Computer Simulation of Polymers on September 11-14, 1989 at Miami Beach.

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Molecular dynamics simulation, polypropylene, structural relaxations.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The molecular dynamics simulation technique (canonical, isobaric ensemble) has been used to investigate the structural characteristics of a model for atactic polypropylene which was generalized from the static energy minimization model of Theodorou and Suter [*Macromolecules*, 18, 1467 (1985)]. Relaxed structures at temperatures above and below Tg were generated by means of a sequence of heating and stress relaxation steps starting from configurations of static energy minimized RIS polymer chains. The detailed microstructure of the simulated polymer was studied by use of bond length, bond angle, and torsion angle distributions and by Voronoi tessellation of the simulation volume. Results indicated there are significant structural differences between the glass and liquid state and that these differences can be used to explain the observed changes in properties which occur at the glass transition.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: Dr. Kenneth Wynne	22b TELEPHONE (Include Area Code): (202) 696-4410 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

(To be filled in by Division)

Paper number as listed on program _____

[A] DIVISION OF: Polymer Chemistry

[B] TITLE OF PAPER: Molecular Dynamics Simulation of Atactic Poly(propylene): Structural Differences between the Liquid and Glass State

Time Required for Presentation _____

☐ Poster Presentation Preferred

[C] AUTHORS (Underline name of speaker)	[D] Business Mailing Address Including Zip Code and telephone Number (List Address only once if all authors at same address.)	[E] ACS Member?	Division Member?	[F] American Chemist or Chemical Engineer? (If not, give classification such a biologist, physicist, etc. Ph.D?
M.F. Sylvester S. Yip A.S. Argon	Massachusetts Institute of Technology 77 Massachusetts Ave. Room 1-306 Cambridge, MA 02139	☒ Yes ☐ No	☒ Yes ☐ No	☐ Chemist ☐ Chemical Engineer Other Polymer Scientist

NOTE: All presenting authors must register for the meeting—either full meeting registration or one-day registration for the day of presentation.

[G] Work done at M.I.T.

[H] Plan ACS ___ nonACS yes publication. Where? Undecided No ___ Uncertain ___

[I] Specify Equipment Required for Presentation *Other than* 2" × 2" slide or overhead (transparency) projector none

[J] ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate full address w/zip code. SINGLE SPACE, BLACK CARBON RIBBON.

DO NOT USE →

MOLECULAR DYNAMICS SIMULATION OF ATACTIC POLY(PROPYLENE): STRUCTURAL DIFFERENCES BETWEEN THE LIQUID AND GLASS STATE. M. F. Sylvester, S. Yip, A.S. Argon, Departments of Mechanical and Nuclear Engineering, M.I.T., Cambridge, Massachusetts 02139.

The molecular dynamics simulation technique (canonical, isobaric ensemble) has been used to investigate the structural characteristics of a model for atactic polypropylene which was generalized from the static energy minimization model of Theodorou and Suter [*Macromolecules*, 18, 1467 (1985)] Relaxed structures at temperatures above and below T_g were generated by means of a sequence of heating and stress relaxation steps starting from configurations of static energy minimized RIS polymer chains. The detailed microstructure of the simulated polymer was studied by use of bond length, bond angle, and torsional angle distributions and by Voronoi tessellation of the simulation volume. Results indicated there are significant structural differences between the glass and liquid state and that these differences can be used to explain the observed changes in properties which occur at the glass transition.

DO NOT USE →

[K] MAIL ABSTRACT TO PERSON NAMED IN ACS DIVISIONAL DEADLINES PUBLISHED (JUNE & DEC.) IN C&EN

On the other hand, the breadth of the volume distributions for the two groups did not increase equally. The standard deviation of the achiral segment volume distribution increased by 7% whereas the chiral group distribution widened by 15%. It can be seen in Figures 2 and 3 that the largest achiral segments found are about 70 Å^3 at both 233°K and 393°K. On the other hand, the maximum size of chiral segments increases from ~70 Å^3 to more than 90 Å^3. The smallest segment volumes found did not significantly change for either type of segment. It appears that raising the temperature induced the formation of a fraction of chiral segments with an exceptionally large volume available to them.

Figure 3: Segment Volume Distribution at 393°K

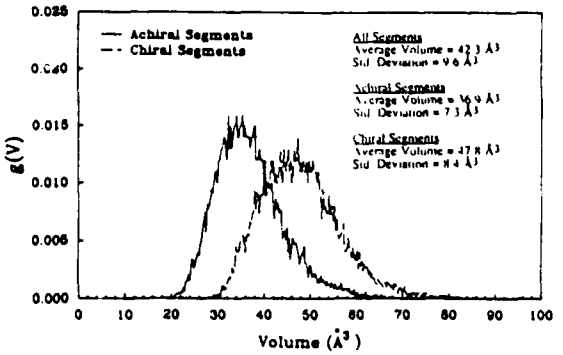


Table I presents the average volume of the chain segments which are first neighbors of achiral and chiral segments with volumes that put them in the 90th, 95th, and 99th percentiles. This information gives some indication of how these larger sized segments are distributed in space.

Table I

Volume Percentile

	90		95		99	
	achiral	chiral	achiral	chiral	achiral	chiral
233°K	41.5	44.6	42.5	44.6	43.6	45.1
393°K	43.7	45.6	43.9	45.8	44.5	46.1

At 233°K the average volume of the neighbors of the larger segments was somewhat larger than the average for segments as a whole (39.0 Å^3; Figure 2). This indicates that the segments with the largest volumes tended to be associated with other segments of larger than average volume.

At 393°K it was also found that the largest segments cluster with segments of greater than average volume (42.3 Å^3; Figure 3). However, the amount by which the average volume of nearest neighbor segments was enhanced appears to be less than that at 233°K. This implies the extent to which clustering occurs is reduced at the elevated temperature.

These findings agree with those of Deng *et al.* [11] Working with an idealized two dimensional model of a simple atomic glass, they found that the tendency of atoms representing an excess of "free volume" to segregate into distinct islands was greater below the glass transition than in the melt.

The segmental mobility at 233°K was found to be several orders of magnitude lower than that at 393°K. [2] The observed differences in the structure at the two temperatures can be used to explain this observation qualitatively.

The calculated Van der Waals (0°K) volume of the achiral CH_2 group is 19.18 Å^3 while that of the chiral CHR group is 38.21 Å^3. From Figures 2 and 3 it can be seen that virtually all of the achiral groups have more than their Van der Waals volume associated with them, while a significant portion of the chiral groups have less than their Van der Waals volume available to them. Presumably, this indicates that the achiral groups are relatively free to move while the chiral groups are more constrained. The major impediment to large scale motion of the polymer backbone therefore seems to be the chiral groups.

At 233°K, 22% of the chiral groups have less than their Van der Waals volume. These groups are so constrained by their neighbors that they are most likely unable to undergo translations or rotations. The average length of chain between these locked groups is ~3 repeat units. It has been postulated on the basis of mechanical models of polymer chains and other considerations, that the smallest length of unconstrained chain which can engage in displacement inducing rearrangements (i.e. chain mobility) is 2-4 repeat units. [9, 10] If this is so, then at 233°K a limited number of rearrangements, which can yield only small segment displacements, are available to the unconstrained lengths of the chain. The mobility of the segments will therefore be low.

At 393°K, however, only 10% of the chiral groups have less than their Van der Waals volume. The average length of chain between locked groups is consequently ~7 repeat units. The number of rearrangements possible and size of the displacements they produce are increased dramatically and hence the segmental mobility is likewise enhanced.

Acknowledgments

The support of the DARPA/URI program through ONR Contract N00014-86-K-0768 is gratefully acknowledged. The authors thank U. W. Suter and M. Hutnik for fruitful discussions and P. H. Mott for invaluable assistance with the Voronoi tessellation.

References

1. Cohen, M.H. and Turnbull, D.; *J. Chem. Phys.* **31**, 1164 (1959).
2. Sylvester, M.F., Yip, S., and Argon, A.S.; *Submitted for publication.*
3. Theodorou, D. and Suter, U.W.; *Macromolecules* **18**, 1467 (1985).
4. Nosé, S.; *J. Chem. Phys.* **81**, 511 (1984).
5. Andersen, H.C.; *J. Chem. Phys.*,**72**, 2384 (1980).
6. Parrinello, M. and Rahman, A.; *J. Appl. Phys.*,**52**, 7182 (1981).
7. Tanemura, M., Ogawa, T., and Ogita, N.; *J. Comput. Phys.*, **51**, 191 (1983).
8. Flory, P.J., Sundararajan, P. R., and DeBolt, L.C.; *J. Am. Chem. Soc.*, **96**, 5015 (1974).
9. Yannas, I.V. and Luise, R.R.; *J. Macromol. Sci. Phys. B.*, **21**, 343 (1982).
10. Robertson, R.E.; *J. Poly. Sci.: Poly. Symp.*, **63**, 173 (1978).
11. Deng, D., Argon, A.S., and Yip, S.; *Accepted for publication , The Philosophical Transactions of the Royal Society of London.*

Molecular Dynamics Simulation of Atactic Poly(propylene): Structural Differences Between the Liquid and Glass State

Mark F. Sylvester, Sidney Yip, and Ali. S. Argon
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Introduction

The glass transition is perhaps the single most profound event occurring in polymers. Despite this, it is still poorly characterized in all but a phenomenological manner. In particular, understanding of how the structure of a polymer glass differs from that of the liquid is limited to the somewhat vague concept of "free volume." [1] It is not known how the volume associated with atoms might be distributed within the polymer or how changes in the distribution are related to the property changes seen at the glass transition. In addition, what other structural changes occur on passing between the liquid and glass states are not known.

We have previously reported on a molecular dynamics model of amorphous atactic poly(propylene) at constant temperature and pressure/stress. [2] Initial results showed that a variety of experimental thermodynamic, structural, and transport properties of the polymer in both the liquid and glass states could be obtained with reasonable accuracy. We now describe the use of the model in studying the detailed microstructure of the polymer liquid and glass.

Methodology

The polymer model is based on the static model of atactic poly(propylene) developed by Theodorou and Suter. [3] It consists of a single polymer chain of degree of polymerization 76 packed in a simulation cell with periodic boundary conditions. Hydrogen atoms along the backbone are treated explicitly, while a unified atom approximation is made for the pendant methyl group. Realistic potentials are used for bond stretching and bending, intrinsic barriers to rotation about backbone bonds, and nonbonded dispersion forces. Parameters for the potentials are based on structural and spectroscopic data on hydrocarbons. Simulation under constant temperature is achieved using the technique of Nosé [4], while constant pressure or stress simulation is carried out using the methods of Andersen [5] or Parrinello and Rahman [6], respectively. Further details of the simulation may be found in the previous paper. [2]

Initial polymer structures above (393°K) and below (233°K) the experimental glass transition (253°K) were prepared using the energy minimization procedure of Theodorou and Suter [3] at the experimental polymer density for the two temperatures of interest. The atomic coordinates of the minimized chains, equivalent to a system at 0°K, were used as input to the molecular dynamics simulation. The simulated chains were brought to thermal equilibrium at either 233°K or 393°K by first carrying out a 10-15 ps microcanonical simulation with occasional velocity rescaling to bring the system temperature to approximately the correct value, followed by a 15-20 ps canonical simulation, followed by a 70 ps isothermal-isobaric simulation. The phase space trajectory of the chain under isothermal-isobaric conditions was then recorded for 20 ps and analyzed.

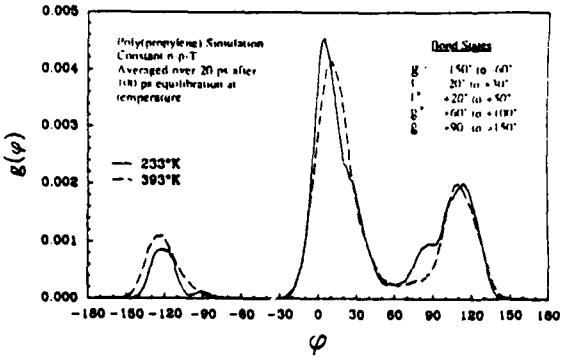
The microstructure of the polymer was probed by determining the Voronoi polyhedra [7] associated with each atom. The polyhedra of the atoms affiliated with each chain segment (i.e. CH_2 or CHR group) were joined together. The distribution of the volume contained in each type of segment polyhedra (achiral and chiral) was computed. As measure of the tendency for large polyhedra to cluster, the volume distribution of first neighbors of those polyhedra whose volume was in the 90th, 95th, and 99th percentiles were evaluated. In addition, the distributions of bond lengths, bond angles and backbone torsional angles were calculated from the atomic coordinates.

Results and Discussion

No significant differences were found between the average bond lengths and bonds angles in the polymer structure at 393°K and 233°K. However the distribution of bond lengths and angles was found to be ~30% wider at 393°K than at 233°K. This is consistent with the increased motion of the atoms at the higher temperature.

Figure 1 shows the distribution of torsional angles, defined according to Flory's convention [8]. Substantial differences can be seen in the distribution at 233°K and that at 393°K. An enhancement of the fraction of torsional angles in the higher energy g^- and t^* states occurs at the expense of the t and g^* states.

Figure 1: Distribution of Torsional Angles



The distributions of Voronoi polyhedra for achiral and chiral chain segments at 233°K and 393°K are shown in Figures 2 and 3, respectively. The distributions are broad and asymmetric, with pronounced tails at large volumes. As expected, the average volume occupied by the chiral CHR chain segments is larger than that taken up by the achiral CH_2 groups.

On raising the temperature from 233°K to 393°K, there were substantial changes in the distributions. The total volume of the simulated polymer was found to increase by 8.6%. The average volume of the achiral segment polyhedra increased by 9.3%, while that of the chiral segment polyhedra was raised by 8.1%. This slight difference is probably insignificant and indicates that both types of segments contributed equally to the volume expansion.

Figure 2: Segment Volume Distribution at 233°K